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Mazyar

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(54) **SYSTEM FOR INCREASING SWELLING EFFICIENCY**

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See application file for complete search history.

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(57) **ABSTRACT**

A swellable system reactive to a flow of fluid including an article having a swellable material operatively arranged to swell upon exposure to a flow of fluid containing ions therein. A filter material is disposed with the swellable material and operatively arranged to remove the ions from the flow of fluid before exposure to the swellable material.

18 Claims, 2 Drawing Sheets

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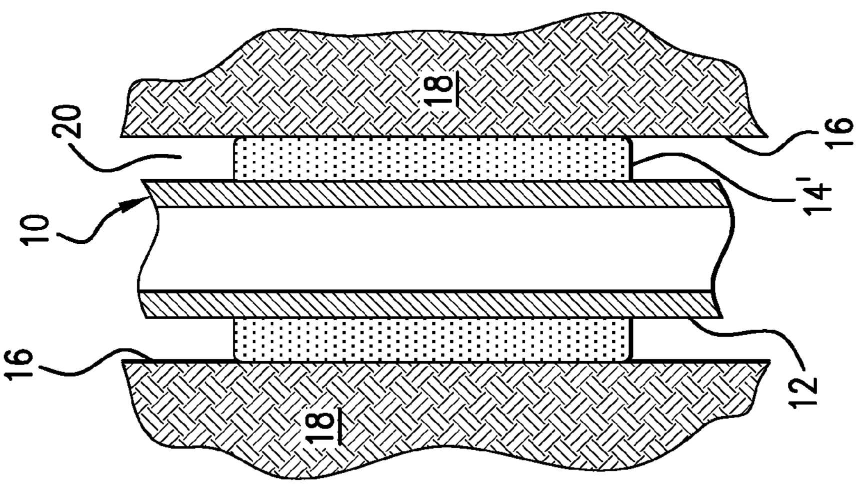

FIG.2

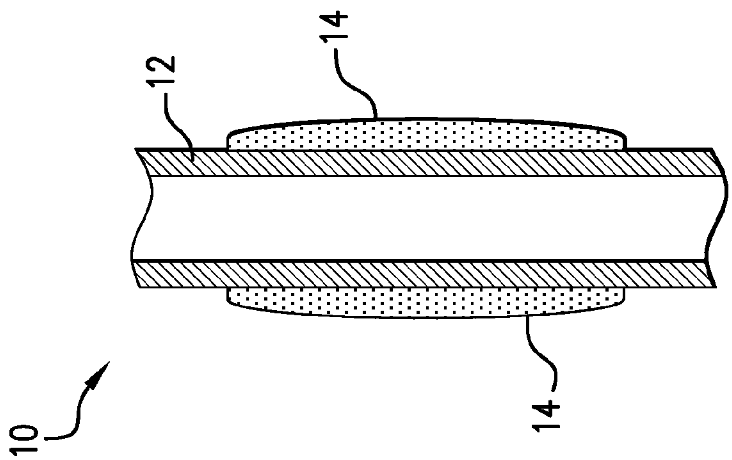

FIG.1

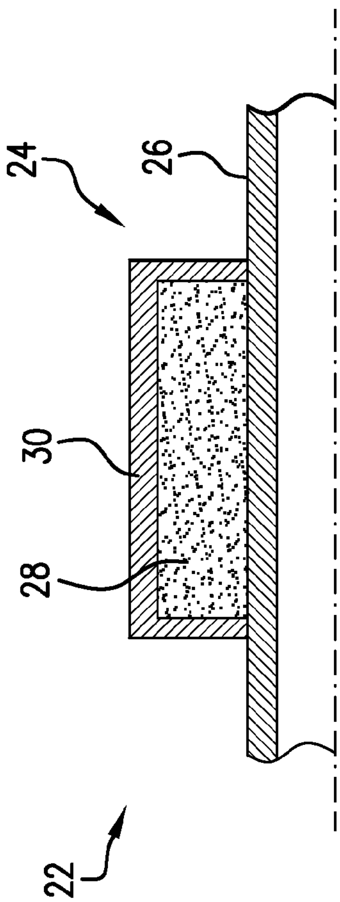

FIG.3

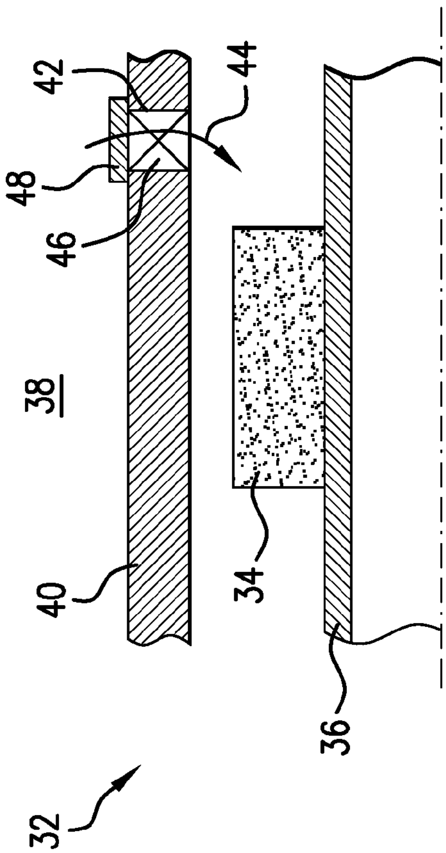

FIG.4

SYSTEM FOR INCREASING SWELLING EFFICIENCY

CROSS REFERENCE

This application is a continuation-in-part of U.S. Non-provisional application Ser. No. 13/300,916 filed on Nov. 21, 2011.

BACKGROUND

Isolation of downhole environments depends on the deployment of a downhole tool that effectively seals the entirety of the borehole or a portion thereof, for example, an annulus between a casing wall and production tube. Swellable packers, for example, are particularly useful in that they automatically expand to fill the cross-sectional area of a borehole in response to one or more downhole fluids. Consequently, swellable packers can be placed in borehole locations that have a smaller inner diameter than the cross-sectional area of the fully expanded swellable packer. However, certain downhole conditions, such as the presence of monovalent and polyvalent cations (e.g., Ca^{2+}, Zn^{2+}, etc.) in the aqueous downhole fluids contacting the swellable packer, tend to decrease both the amount of swelling and the rate at which the packer swells, and may also accelerate degradation of the packer. In order to overcome these issues and to continually improve upon swelling efficiency under a variety of conditions, the industry is always desirous of new and alternate swelling systems.

SUMMARY

A swellable system reactive to a flow of fluid, including an article including a swellable material operatively arranged to swell upon exposure to a flow of fluid, the flow of fluid containing ions therein; and a filter material disposed with the swellable material and operatively arranged to remove the ions from the flow of fluid before exposure to the swellable material.

A method of operating a swellable system including filtering ions from a flow of fluid with a filter material; and swelling a swellable material responsive to the flow of fluid upon exposure to the fluid.

BRIEF DESCRIPTION OF THE DRAWINGS

The following descriptions should not be considered limiting in any way. With reference to the accompanying drawings, like elements are numbered alike:

FIG. **1** is a cross-sectional view of a swellable article in an initial configuration;

FIG. **2** is a cross-sectional view of the swellable article of FIG. **1** in a swelled configuration;

FIG. **3** is a swellable system according to an embodiment disclosed herein where a swellable article is disposed with a filter material in a shell covering a swellable core; and

FIG. **4** is a swellable system according to another embodiment disclosed herein where a filter material is separately disposed from a swellable article.

DETAILED DESCRIPTION

A detailed description of one or more embodiments of the disclosed apparatus and method are presented herein by way of exemplification and not limitation with reference to the Figures.

Referring now to FIG. **1**, a system **10** including a tubular or string **12** and a downhole article **14**, e.g., a packer or sealing element, disposed thereon is illustrated. The downhole article **14** includes, for example, a base composition and a filter component, discussed in more detail below. The base composition comprises an elastomeric material and/or an absorbent material. Due to fluid absorption by the absorbent material, e.g. absorption of water, brine, hydrocarbons, etc., the article **14** expands or swells to a second configuration shown in FIG. **2**. Various absorbent materials are known and used in the art. For example, with respect to water swellable embodiments any so-called Super Absorbent Polymer could be used, or those marketed by Nippon Shokubai Co., Ltd. under the name AQUALIC® CS-6S. The elastomeric material is included, for example, to provide a seal against a downhole structure **16**, e.g., a borehole in a subterranean formation **18**, shown in FIG. **2**. Of course, the structure **16** could be any other tubing, casing, liner, etc. located downhole and engagable by the article **14**. The elastomeric material could be any swellable or non-swellable material. In some embodiments, the elastomeric material is absorbent with respect to one or more downhole fluids thus also encompassing the absorbent material. In this way, for example, the article **14** can be run-in having an initially radially compressed configuration, exposed to fluids once located downhole, and expanded to engage between the tubular **12** and the structure **16**. In one embodiment, the structure **16** is isolated by expansion of the article **14** such that fluids (e.g., from the formation **18**) are substantially prevented from flowing past the article **14** once the article **14** is expanded.

Downhole fluids typically comprise an aqueous component, which more accurately is a brine containing various ions, e.g., metal cations from dissolved salts. As noted above, monovalent and polyvalent cations can interact with the absorbent material, and decrease the overall rate and ratio of expansion of the absorbent material, thereby hindering the sealing efficacy of the article. It has been generally found that polyvalent cations such as Ca^{2+}, Zn^{2+}, etc. have a more profound effect on the performance of swellable materials, particularly in water swellable articles, than monovalent cations and are thus usually more desirable to be removed. It is to be appreciated that while water-swellable materials are discussed as an exemplary embodiment that is adversely affected by the presence of cations, other materials may be swellable in response to different fluids and/or adversely affected by anions. For example, in one embodiment the swellable material is adversely affected (e.g., reduced swelling, shorter life span, slower swelling rate, etc.) by the presence of anions. For this reason, the term "ions" as used herein will refer to any cation or anion that has a negative effect on the performance of a corresponding swellable material.

To mitigate the deleterious effect of such ions on the absorbent material, the filter material acts to remove or filter ions from the downhole fluids before they interact with the swellable material. By remove or filter, it is meant that the filter material captures or holds the ions in, at, or proximate a capture site or location proximate to the filter material, or otherwise neutralizes the ions such that the flow of fluid is at least partially relatively devoid of ions downstream of the filter material. Thus, while the ions are still technically in the fluid, they are prevented from adversely affecting the swelling of the swellable material and therefore considered to be removed or filtered. The removal, filtering, or capture may be done by chemical or physical bonding between the filter material and the ions, physisorption or chemisorption at or by the filter material or a surface thereof, electrostatic and/or van der Waals attraction between the filter material or an atomic structure thereof (e.g., functionalized group) and the ions, etc., examples of which are discussed in more detail below.

In the embodiment of FIGS. **1** and **2**, the filter material, the elastomeric material, and/or the absorbent material can all be mixed together, e.g., homogeneously, then formed into the article **14**. An alternate embodiment for a system **22** is shown in FIG. **3**, the system **22** including an article **24** on a tubular or string **26**. The article **24** is formed from a core **28** and a shell **30**. In this embodiment, the core **28** includes the aforementioned swellable material, while the shell **30** includes the filter material. The core **28** and the shell **30** may both, for example, include suitable elastomeric and/or filler materials to provide sealing for the article **24** and to impart chemical and physical properties to the article **24**. In this way, the flow of fluid to which the swellable material in the core **28** is reactive will first be filtered of ions by the filter material in the shell **30**.

A system **32** according to another embodiment is shown in FIG. **4** in which a swellable article **34** is disposed with a tubular or string **36**. In this embodiment, a formation **38** is separated from the article **34** by a radially disposed tubular or string **40**, e.g., a casing, liner, tubing, etc. The tubular/string **40** includes at least one port or opening **42** for enabling a flow of fluid, generally designated by an arrow **44**, to encounter the article **34**. The filter material can be arranged in a plug **46** positioned in the opening **42**, in a membrane or film **48** positioned over the opening **42**, etc. The plug **46** can be formed as any suitable fluid permeable member for creating a passageway for communicating fluid to the swellable material. In this way, the flow of fluid is filtered by the filter material before it reaches the article **34**. The plug **46** and/or the membrane **48** could be formed from any suitable permeable material, e.g., a porous foam, fibers, with the filter material disposed in or with the permeable material, e.g., in pores of the permeable material.

In another embodiment, essentially a combination of the above, the shell **30** could be a protective or elastomeric shell impermeable to downhole fluids and resistant to corrosion and degradation. A permeable plug, such as discussed with respect to the plug **46** could be included in the shell **30** as opposed the an outer tubular **40**. In this way, the swellable article will benefit from an outer shell made of an elastomeric or other material that can be selected to provide beneficial properties such as corrosion resistance, fluid impermeability, etc., while also maintaining the advantageous ion filtering properties provided by the current invention as discussed herein.

In one embodiment, the filter material comprises one or more graphene-based compounds. By graphene-based it is meant a compound that includes or is derived from graphene, such as graphene itself, graphite, graphite oxide, graphene oxide, etc. The compounds could take any form used with such graphene-based compounds, such as sheets or nanosheets, particles, flakes, nanotubes, etc. Advantageously, the unique properties of graphene enable effective donor—acceptor interactions between both the anions and the cations and the graphene flakes or particles. The graphene-based materials, associated oxides, or other derivatives or functionalized compounds thereof may contain a corresponding relatively large number of capture sites for attracting and binding ions via van der Waals and/or Coulombic interactions. Of course, other materials with electron-rich surfaces can be used for similarly filtering cations, while highly electron deficient materials may be utilized with respect to anions.

To further increase the ability of graphene-based filter materials to capture the aforementioned polyvalent cations, the filter materials can be functionalized to include one or more functional groups. The process of forming graphite or graphene oxide, for example, results in the inclusion of various functional groups that are relatively negatively charged (e.g., carboxylic acid groups) or polar (e.g., carbonyl groups). Polyvalent cations will be attracted to and captured by these groups. In one embodiment the filter material is covalently modified with thiol groups according to known diazonium chemistry procedures. Thiol groups are naturally excellent at capturing positively charged ions, notably doubly charged mercury cations, although other metallic cations ions such as the aforementioned Ca^{2+}, Zn^{2+}, etc., contained in downhole brines will also be readily captured by thiol groups. Other functional groups such as disulfide groups, carboxylic acid, sulfonic acid groups may also be used for their ability to capture polyvalent cations, particularly doubly charged cations. Other functional groups include chelating ligand groups, such as iminodiacetic acid, iminodiacetic acid group, N-[5-amino-1-carboxy-(t-butyl)pentyl]iminodi-t-butylacetate) group, N-(5-amino-1-carboxypentyl)iminodiacetic acid group, N-(5-amino-1-carboxypentyl)iminodiacetic acid tri-t-butyl ester group, aminocaproic nitrilotriacetic acid group, aminocaproic nitrilotriacetic acid tri-tert-butylester group, 2-aminooxyethyliminodiacetic acid group, and others that would be recognized by those of ordinary skill in the art in view of the disclosure herein.

The graphene-based materials could also be functionalized to filter anions, e.g., with quaternary ammonium, quaternary phosphonium, ternary sulfonium, cyclopropenylium cations, or primary, secondary, ternary amino, or other groups. These groups are either positively charged or become protonated in acidic environments and thus require anions to compensate for the charge. In some situations, the anion can be exchanged with another anion while preserving charge. For example, in one embodiment, the graphene-based material is functionalized with a quaternary ammonium group, the positive charge of which is balanced by hydroxide anions. In this example, in brine containing SO_4^{2-} anions, one SO_4^{2-} anion will be captured and two hydroxide anions (OH^-) will be released. In an embodiment, a mixture of graphene-based material functionalized with sulfonic acid groups and graphene-based material functionalized with quarternary ammonium groups balanced by hydroxide anions is used to neutralize a $CaCl_2$ brine. In the cation-exchange process, Ca^{2+} cations are captured with a simultaneous release of two H^+ ions for each Ca^{2+} cation. In the anion-exchange process, Cl^- ions are captured by the quaternary ammonium group with a simultaneous release of OH^- anion for each Cl^- ion. Recombination of released H^+ and OH^- ions results in the formation of water molecules, which may contribute to the swelling process of water-swellable materials.

While the invention has been described with reference to an exemplary embodiment or embodiments, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiment disclosed as the best mode contemplated for carrying out this invention, but that the invention will include all embodiments falling within the scope of the claims. Also, in the drawings and the description, there have been disclosed exemplary embodiments of the invention and, although specific terms may have been employed, they are unless otherwise stated used in a generic and descriptive sense only and not for purposes of limitation, the scope of the invention therefore not being so limited. Moreover, the use of the terms first, second, etc. do not denote any order or importance, but rather the terms first, second, etc. are used to distinguish one element from another. Furthermore, the use of the terms a, an, etc. do not denote a limitation of quantity, but rather denote the presence of at least one of the referenced item.

What is claimed is:

1. A swellable system reactive to a flow of fluid, comprising:

an article including a swellable material operatively arranged to swell upon exposure to the flow of fluid, the fluid being aqueous and containing metallic cations from dissolved salts; and

a filter material disposed with the swellable material and operatively arranged to remove the polyvalent cations from the flow of fluid before exposure to the swellable material,

the filter material comprising a graphene-based material, the graphene-based material comprising at least one functional group operatively arranged to capture the polyvalent cations;

wherein the filter material and the swellable material are mixed homogeneously in the article.

2. The system of claim **1**, wherein the filter material exerts van der Walls forces, Coulombic forces, or combinations thereof on the ions.

3. The system of claim **1**, wherein attraction between the filter material and the ions is formed by functional groups attached to the filter material.

4. The system of claim **3**, wherein the functional groups are thiol groups, disulfide groups, carboxylic acid groups, sulfonic acid groups, chelating ligand groups, or a combination including at least one of the foregoing.

5. The system of claim **1**, wherein the polyvalent cations are di-valent metallic cations.

6. The system of claim **1**, wherein the graphene-based material is graphene, graphite, graphene oxide, graphite oxide, or a combination including at least one of the foregoing.

7. The system of claim **6**, wherein the at least one functional group is a thiol group, a disulfide group, a carboxylic acid group, a sulfonic acid group, a chelating ligand group, or a combination including at least one of the foregoing.

8. The system of claim **1**, further comprising an elastomeric material operatively arranged to enable the article to seal against another structure after swelling.

9. The system of claim **1**, wherein the filter material is operatively arranged to remove the metallic cations by capturing the metallic cations, capturing the metallic cations while simultaneously releasing one or more other ions in order to preserve a charge balance, or a combination including at least one of the foregoing.

10. A method of operating a swellable system of claim **1** comprising:

removing metallic cations from a flow of fluid with a filter material; and

swelling a swellable material responsive to the flow of fluid upon exposure to the fluid.

11. The method of claim **10**,

wherein the metallic cations are polyvalent metallic cations.

12. The method of claim **10**, wherein the filter material comprises a graphene-based material being graphene, graphite, graphene oxide, graphite oxide, or a combination including at least one of the foregoing.

13. The method of claim **12**, wherein the graphene-based material further comprises at least one functional group operatively arranged to capture the ions.

14. The method of claim **13**, wherein the at least one functional group is a thiol group, a disulfide group, a carboxylic acid group, a sulfonic acid group, a chelating ligand group, or a combination including at least one of the foregoing.

15. The method of claim **13**, wherein the at least one functional group is a quaternary ammonium group, a quaternary phosphonium group, a ternary sulfonium group, a cyclopropenylium cation, a group configured to be protonated in an acidic environment, a primary amino group, a secondary amino group, a ternary amino group, or a combination including at least one of the foregoing.

16. The system of claim **10**, wherein removing the metallic cations includes capturing the ions metallic cations, capturing the metallic cations while simultaneously releasing one or more other in order to preserve a charge balance, or a combination including at least one of the foregoing.

17. The system of claim **1**, wherein the at least one functional group is a thiol group, a disulfide group, or a combination including at least one of the foregoing.

18. The system of claim **1**, wherein the at least one functional group is a chelating ligand group.

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